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COMPLETE SPECIFICATION

A Continuous Process for preparing Meta Di-Isopropylbenzene

We, N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing meta-di-isopropyl-benzene either as such or in admixture with para-di-isopropylbenzene. In the latter case, the two components can readily be separated by distillation.

Meta-di-isopropylbenzene is a valuable initial material for the preparation of a number of important products such as isophthalic acid, the esters of which are used as initial materials for the preparation of plasticizers and synthetic fibres. The oxidation to isophthalic acid may be effected, for instance, in a manner similar to that described in our copending British Patent Applications Nos. 30687/53 (Serial No. 737,439); 32987/54; and 4321/55 (Serial Nos. 770,224 and 772,635). If desired, meta-di-isopropylbenzene may also be converted into the mono- or di-hydroperoxides which yield on decomposition, among other substances, meta-isopropyl phenol and resorcinol respectively, in addition to acetone.

According to the present invention a continuous process for preparing meta-di-isopropylbenzene comprises alkylating benzene or cumene or a mixture of benzene and cumene to form an alkylation product containing ortho-, meta- and para-di-isopropylbenzenes together with benzene derivatives containing more than two isopropyl groups in their molecules, removing a fraction containing ortho- and meta-di-isopropyl benzenes from said alkylation product, contacting said fraction with a silicate catalyst to effect isomerization, and separating by distillation an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer from the resulting isomerisation product.

Preferably a fraction comprising said benzene derivatives containing more than 2 isopropyl groups in their molecules is also removed from said alkylation product and is contacted with a silicate catalyst in admixture with at least an equimolar amount of either benzene or cumene or both benzene and cumene to effect transalkylation, and an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer is then separated by distillation from the resulting transalkylation product.

The process of the present invention makes use of the discovery that in both the isomerization and the trans-alkylation the ortho-di-isopropyl-benzene is converted preferentially.

In general in carrying out the process of the present invention, the alkylation product is separated into the above-mentioned fractions, and the mixture of ortho- and meta-di-isopropylbenzenes is passed to an isomerization reactor in which it is subjected to isomerization in the presence of a silicate catalyst (as hereinafter described); such catalysts may also be referred to as cracking catalysts since they are also suitable for use as catalysts in the cracking of petroleum. The mixture leaving the isomerization reactor consists of benzene, cumene, a mixture of di-isopropyl benzene isomers which is substantially free from ortho di-isopropyl benzene, and compounds containing more than two isopropyl groups per molecule.

An analogous mixture is obtained by the transalkylation with either benzene or cumene or both benzene and cumene of the fraction consisting of the benzene derivatives with more than two isopropyl groups per molecule, in the presence of a silicate catalyst.

The two reaction mixtures obtained from the isomerisation and transalkylation reactors respectively will generally be combined and the combined mixture thereafter separated by distillation into benzene, cumene, a substantially ortho-free meta-di-isopropylbenzene fraction, and a fraction consisting of para-di-isopropylbenzene and compounds having more than two isopropyl groups per molecule, which latter compounds will often be briefly referred

to in the following description as "higher alkylated products".

It is also possible to separate a fraction comprising the para-di-isopropylbenzene together with the meta-isomer, and possibly small quantities of the ortho-isomer, from the reaction mixtures derived from the isomerization and transalkylation reactors, the higher alkylated products then being obtained as the highest-boiling fraction from these reaction mixtures. If desired the fraction consisting of di-isopropylbenzene isomers may be separated by distillation into the para-isomer on the one hand and substantially ortho-free meta-isomer on the other.

In most instances the cumene and benzene will be recycled to for instance the alkylator and the transalkylator and the mixture consisting of para-di-isopropylbenzene and the higher alkylated products may be recycled to that distillation column in which such components are separated from each other during the separation of said alkylation product.

In the process of the present invention it is also possible for all or part of the mixture of ortho- and meta-di-isopropylbenzene to be led to the transalkylator in which they are transalkylated in contact with a silicate catalyst either alone or jointly with the higher alkylated products. Thus according to one modification of the process of the present invention said fraction containing ortho- and meta-di-isopropylbenzenes removed from said alkylation product is contacted with a silicate catalyst in admixture with at least an equimolar amount of either benzene or cumene or both benzene and cumene to effect transalkylation, and an ortho- and meta-di-isopropyl-benzenes fraction consisting substantially entirely of the meta isomer is separated by distillation from the resulting transalkylation product.

Although in most cases the para-di-isopropylbenzene which is produced in the alkylation stage of the present process is also valuable in view of the possibility of converting it into terephthalic acid, in certain circumstances a higher yield of the meta-isomer may nevertheless be preferred and in such case the process of the present invention can be carried out in such a manner that the para-di-isopropyl-benzene is transalkylated in the presence of a silicate catalyst and either wholly or partly, either separately or together with the ortho- and meta-di-isopropylzenzene mixture and/or the higher alkylated products, or the para-isomer is isomerized in the presence of a silicate catalyst either separately or together with the ortho- and meta-di-isopropyl benzene mixture.

It is also possible to carry out the process of the present invention by contacting either all or part of the above-mentioned fractions removed from said alkylation product with a silicate catalyst to effect de-alkylation, the fractions being treated either individually or in a combination of two or more fractions, after which the de-alkylation product, which has a composition similar to those of the reaction products from the isomerization and transalkylation reactors, is separated into the above-mentioned ortho-and meta-di-isopropyl-benzenes fraction in the manner indicated. Thus according to a further modification of the process of the present invention ortho- and meta-di-isopropylbenzenes, para-di-isopropylbenzene, and benzene derivatives containing more than 2 isopropyl groups in their molecules are removed from said alkylation product either as three separate fractions or as one or more mixed fractions, said separate or mixed fractions are contacted with a silicate catalyst to effect alkylation, and an ortho- and meta-di-isopropylbenzenes fraction consisting substantially of the meta isomer is then separated by distillation from the resulting de-alkylation product(s).

Unlike the alkylation, isomerization and transalkylation reactions, which are preferably carried out in the liquid phase, the de-alkylation is a gas phase reaction. Consequently, since it is usually less desirable to combine a gas phase reaction with other operations involving exclusively or mainly liquid phase reactions, the de-alkylation will as a rule not be applied. Moreover undesired decomposition products such as propane and xylenes are formed, particularly at higher temperatures, e.g. above 425° C. However, since in the present case de-alkylation of the higher alkylated products need only proceed as far as the di-isopropylbenzene, it is possible to operate with somewhat lower temperatures e.g. 300—350° C., so that only very few by-products are formed, especially when SiO_2—MgO containing catalysts are used.

The preferential conversion of ortho-di-isopropylbenzene during isomerization, transalkylation and de-alkylation in the presence of a silicate catalyst is of particular importance in the preparation of meta-di-isopropylbenzene, since these ortho- and meta-isomers cannot be economically separated by distillation or by any other known method.

In view of this it is also impossible simply to combine the fractions which contain ortho- and meta-di-isopropylbenzenes and which are obtained by distillation of the reaction mixtures derived by alkylation on the one hand and by contact with a silicate catalyst under de-alkylation, isomerization or transalkylation conditions on the other hand, because in most cases the fraction derived from the alkylation is richer in ortho-di-isopropylbenzene than the said other fractions, unless the alkylation is carried out under such conditions and with the use of such catalyst that isomerization and transalkylation take place at the same time. This is the case, for example, when $AlCl_3$ is used as a catalyst.

The slight quantity of ortho-isomer which

is present in the crude meta-isomer as obtained from the reaction mixture derived from the de-alkylation, isomerization or transalkylation, is no obstacle to pure isophthalic acid being obtained by subsequent oxidation thereof, since the ortho-isomer is not oxidized to phthalic acid in the oxidation reacion. The isophthalic acid thus obtained may be esterified with alcohols to produce di-alkyl esters, which may be used as initial material for the preparation of plasticizers and synthetic fibres.

It is also possible to carry out the process of the present invention in such a manner as to produce the meta-di-isopropylbenzene in association with the para-isomer, after which the mixture may be oxidized to yield a mixture of iso- and terephthalic acids which may be esterified with a lower alcohol, e.g. methanol, to give di-methyl iso- and terephthalates respectively. Such an ester mixture may be used as initial material for synthetic fibres and plasticizers, even without being split into its component esters.

In the process of the present invention alkylation may be carried out with various alkylating agents, such as, for instance, an isopropyl halide (preferably isopropyl chloride), isopropyl alcohol, or propene, or a gas mixture containing in addition to propene other gases, such as, for instance, a technical propene-propane mixture formed during the cracking of petroleum fractions, which mixture consists of about 60% propene, the remainder being almost exclusively propane.

The catalyst used may be any of the alkylation catalysts known from the literature, such as a catalyst of the Friedel-Crafts type, preferably $AlCl_3$, or concentrated H_2SO_4, HF or a cracking catalyst. Preferably a cracking catalyst of the silicate type is used, that is a silicate catalyst containing in combined form one or more of the metals aluminium, zirconium and magnesium. Thus such silicate catalysts mainly consist of silicon dioxide, with smaller amounts of one or more oxides of metals such as aluminium, zirconium and magnesium, and optionally also calcium, sodium and potassium, which are chemically bound to the silicon dioxide in the form of silicates, also present. Other oxides, e.g. those of hydrogen, carbon, and sulphur, may also occur in a chemically bound form. Usually, however, water is present in the oxide mass in a free or only very loosely bound form. In many instances only traces of certain oxide components occur in the catalysts. The silicate catalysts referred to can be either of natural or synthetic origin.

In carrying out isomerisation, transalkylation or de-alkylation in the process of the present invention catalysts of the aluminium-silicate type are especially preferred, viz. silicate catalysts mainly consisting of Al_2O_3 and SiO_2, while certain other components such as Na_2O, K_2O, CaO, MgO, ZrO_2, H_2O, CO_2 and SO_3 may also occur in combined form in smaller amounts, sometimes traces. These catalysts usually comprise a higher SiO_2 than Al_2O_3 content. A ratio by weight which frequently occurs is, for example, 85—90% by weight of SiO_2 and 15—10% by weight of Al_2O_3.

The process of the present invention may be carried out continuously for example in a manner which will now be described with reference to the accompanying drawings which is a diagrammatic flowsheet of the process:—

A technical mixture of propene and propane such as referred to above is led via a line 1 into an alkylation reactor 4, to which cumene is also introduced via a line 2. If desired the cumene may be mixed with benzene introduced into the line 2 via a line 3. The alkylation-reaction mixture leaves the alkylator 4 and flows through a line 5 to a gas stripper 6 in which the unconverted propene and also the propane are separated from the reaction mixture and leave the stripper 6 via a line 7. Any propene present in the gases withdrawn through the line 7 may be separated therefrom and recycled to the line 1.

The reaction mixture freed from propene and propane leaves the stripper 6 via a line 8 and flows to a distillation column 9 in which unconverted benzene is removed as top product and recycled to the supply line 3 via a line 10. The bottom product is led via a line 11 to a distillation column 12 in which cumene is removed as top product and recycled via a line 13 to the line 2.

By starting from cumene instead of a mixture of benzene and cumene the column 9 may be dispensed with and the line 8 directly connected to the column 12.

The bottom product which leaves the column 12 via a line 14 consists of a mixture of ortho-, meta- and para-di-isopropylbenzenes and higher alkylated products. This mixture is introduced into a column 15 in which a mixture of ortho- and meta-di-isopropyl benzene is withdrawn as top product via a line 16 and passed to an isomerization reactor 21. The bottom product of column 15, consisting of para-di-isopropylbenzene and higher alkylated products, is led via a line 17 to a column 18 in which para-di-isopropylbenzene is removed from the column 18 as top product via a line 19 leading to a storage tank 22. The higher alkylated products which leave the column 18 via a line 20 are led into a transalkylator 23, together with at least an equimolar quantity of benzene and/or cumene which is/are introduced into the transalkylation reactor 23 from line 3 via a line 24 and from line 2 via a line 36 respectively.

A reaction product consisting of benzene, cumene, a very slight amount of ortho-di-isopropylbenzene, meta- and para-di-isopropylbenzenes and higher alkylated products, is led from the isomerization reactor 21 via a line 25 into a column 26 from which benzene is withdrawn as top product via a line 27 and re-

cycled to the line 3. The bottom product flows via a line 28 to a column 29, in which cumene is removed as the top product and recycled to the line 2 via a line 30. The bottom product of the column 29 flows via a line 31 to a column 32 from which meta-di-isopropylbenzene, mixed with a very small quantity of the ortho-isomer, is withdrawn as top product via a line 33.

The bottom product of the column 32, consisting of para-di-isopropylbenzene and higher alkylated products, is recycled via a line 34 to the line 17.

The reaction mixture obtained from the transalkylator 23 which contains the same components as the isomerization reaction mixture, is introduced into the line 25 via a line 35. It is also possible for this mixture to be led via the line 35 to a similar series of distillation columns as columns 26, 29 and 32 and individually separated by distillation into fractions as mentioned above in connection with these columns.

The following may be mentioned as a few of the possible variants of the scheme described above:—

It is possible to separate the bottom product derived from column 12 into a fraction consisting of ortho-, meta- and para-di-isopropylbenzenes and a fraction consisting of the higher alkylated products, after which the di-isopropylbenzenes fraction is further separated into a fraction containing the ortho and meta isomers and a fraction comprising the para-isomer.

Furthermore, in the process of the present invention it is possible to de-alkylate the whole or part of the fraction consisting of the higher alkylated products using a silicate catalyst, and to split the product thus obtained, which contains little ortho-di-isopropylbenzene, into its components in the same way as described above for the isomerization and transalkylation product. It is also possible to de-alkylate the whole or part of the higher alkylated products and/or the para-di-isopropylbenzene.

A further variant of the process of the present invention consists in also isomerizing the whole or part of the para-di-isopropyl benzene produced in the alkylation stage of the present process: such isomerization of the para-isomer can be effected either separately or together with the ortho- and meta-isomers.

It is also possible to carry out the transalkylation with the whole or part of the fraction consisting of ortho- and meta-di-isopropylbenzenes either separately or together with the higher alkylated benzenes.

The whole or part of the para-di-isopropylbenzene fraction may be transalkylated either separately or together with the higher alkylated products and/or a fraction containing ortho-and meta-di-isopropylbenzenes.

A further variant may also be made in the manner in which the reaction products obtained in the isomerization, dealkylation and trans-alkylation reactions are worked up, e.g. by separating the mixture from column 29 into a di-isopropylbenzene fraction which is poor in the ortho isomer, and a fraction consisting of the higher alkylated products.

The process of the present invention may be illustrated by the following examples:—

EXAMPLE I.

A feed stock consisting of cumene and propene in the proportion of 6 mols of cumene and 2 mols of propene was led continuously into a stirred autoclave in which the cumene was alkylated, whilst mixing homogeneously, in the presence of a powdery silicate catalyst of the aluminium-silicate type at a temperature of 200° C. under a pressure of 30 atmospheres (absolute) and with a liquid hourly space velocity (LHSV) of 10. For every 6 moles of cumene introduced into the alkylation reactor, 4.334 mols consisted of recycled cumene which had remained unconverted in the alkylation, 0.257 mol consisted of cumene which was formed in an isomerization reactor to be referred to hereinafter, and 1.409 mols consisted of cumene which was prepared in a transalkylation reactor which will also be referred to hereinafter. From the alkylate thus obtained, which was composed of the above-mentioned 4.334 mols of unconverted cumene, 0.666 mol of (ortho+meta)-di-isopropylbenzenes, 0.666 mol of para-di-isopropylbenzene and 0.334 mol of tri-isopropylbenzene, the cumene was separated by distillation and recycled to the alkylation reactor. The remaining reaction mixture was then separated by distillation into a tri-isopropylbenzene fraction (0.334 mol) which was led to the transalkylation reactor, and a mixture of *o*, *m* and *p*-di-isopropylbenzenes (1.332 mols).

To this mixture of di-isopropylbenzene isomers was also added 0.218 mol of para-di-isopropylbenzene derived from the reaction product of the isomerization reactor, and 0.054 mol of para-di-isopropylbenzene, derived from the reaction product of the transalkylation reactor. The mixture of di-isopropylbenzene isomers thus obtained constituted the feed to the above-mentioned isomerization reactor in which the same kind of catalyst was used as in the alkylation, but in which the operation was carried out at a temperature of 240° C., under a pressure of 20 atmospheres (absolute), and with an LHSV of 2. The reaction product withdrawn from the isomerization reactor was then separated by distillation into 0.257 mol of cumene, a mixture of 0.008 mol of ortho- and 0.864 mol of meta-di-isopropylbenzene, 0.218 mol of para-di-isopropylbenzene and 0.257 mol of tri-isopropylbenzene. As indicated previously the cumene (0.257 mol) was recycled to the alkylation reactor, and the para-di-isopropylbenzene (0.218 mol) was recycled to the feed to the isomerization reactor. The

tri-isopropylbenzene (0.257 mol) was led to the transalkylation reactor which employed the same catalyst as in the alkylation. The transalkylation was carried out with the aid of benzene at 300° C., under 30 atmospheres (absolute) pressure and with an LHSV of 1. The above-mentioned tri-isopropylbenzenes (0.334 mol) derived from the alkylation was also led into the transalkylation reactor, while the unconverted fraction which was separated from the transalkylation product and which consisted of tri-isopropylbenzenes (0.020 mol) was recycled to this reactor. The total tri-isopropylbenzenes feed to the transalkylation reactor was thus 0.611 mol and the quantity of benzene added thereto was 3.055 mols, of which 2.056 mols consisted of unconverted benzene. The transalkylation product was separated by distillation into unconverted benzene to be recycled (2.056 mols), 1.409 mols of cumene which as already indicated was led to the alkylation reactor, a mixture of 0.001 mol of ortho- and 0.126 mol of meta-diisopropylbenzene, 0.054 mol of para-di-isopropylbenzene which as previously indicated was led to the isomerization reactor, and 0.020 mol of unconverted tri-isopropylbenzenes which was recycled to the transalkylation reactor. In this way a mixture consisting of 0.864+0.126=0.990 mol of meta-di-isopropylbenzene and only 0.008+0.001=0.009 mol of ortho-di-isopropylbenzene was prepared continuously from 2 mols of propene and 0.999 mol of benzene.

EXAMPLE II.

A further run was made under the same alkylation, isomerization and transalkylation conditions as described in Example I. The alkylation reactor was continuously fed with cumene and propene in the proportion of 2 mols of propene to 3 mols of cumene. Of each 3 mols of cumene, 1.500 mols consisted of recycle cumene derived from the alkylate, 0.160 mol consisted of cumene derived from the isomerization product, and 1.340 mols consisted of cumene formed in the transalkylation. The alkylate was separated by distillation into unconverted cumene to be recycled (1.500 mols), di-isopropylbenzene isomers (1 mol) and tri-isopropylbenzenes (0.500 mol) of which the latter was led to the transalkylation reactor. The separated di-isopropylbenzenes (1 mol) were isomerized as such, the reaction product of the isomerization being separated by distillation into 0.160 mol of cumene to be recycled to the alkylation reactor, a mixture of 0.004 mol of ortho- and 0.540 mol of meta-di-isopropylbenzenes, 0.136 mol of para-di-isopropylbenzene and 0.160 mol of tri-isopropylbenzenes which was led to the transalkylation reactor, together with the above-mentioned tri-isopropylbenzenes (0.500 mol) derived from the alkylate, and the 0.060 mol of tri-isopropylbenzenes which had remained unconverted in the transalkylation.

The total tri-isopropylbenzene feed to the transalkylation reactor was thus 0.720 mol, and the total benzene feed thereto was 2.160 mols, of which 1.160 mols consisted of recycled unconverted benzene. The transalkylate was separated by distillation into the above-mentioned unconverted benzene (1.160 mols), cumene (1.340 mols) which was led to the alkylation reactor, a mixture of 0.002 mol of ortho- and 0.222 mol of meta-di-isopropylbenzenes, 0.096 mol of para-di-isopropylbenzene and 0.060 mol of unconverted tri-isopropylbenzenes which as previously indicated was recycled to the transalkylation reactor.

In this process a mixture of 0.540+0.222=0.762 mol of meta- and 0.004+0.002=0.006 mol of ortho-di-isopropylbenzene, as well as 0.136+0.096=0.232 mol of para-di-isopropylbenzene was continuously prepared from 2 mols of propene and 1 mol of benzene.

In our prior dated U.K. Patent Specifications Nos. 749,186 and 749,187 we claim continuous processes for preparing *p*-di-isopropylbenzene and processes for preparing terephthalic acid from the resulting *p*-di-isopropyl benzene, and it is to be understood that we do not claim herein anything claimed in our Specifications 749,186 and 749,187.

Subject to the foregoing disclaimer what we claim is:—

1. A continuous process for preparing meta-di-isopropylbenzene, which comprises alkylating benzene or cumene or a mixture thereof to form an alkylation product containing ortho-, meta- and para-di-isopropylbenzenes together with benzene derivatives containing more than 2 isopropyl groups in their molecules, removing a fraction containing ortho- and meta-di-isopropylbenzenes from said alkylation product, contacting said fraction with a silicate catalyst to effect isomerisation, and separating by distillation an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer from the resulting isomerisation product.

2. A process as claimed in Claim 1, which comprises removing from said alkylation product a fraction comprising said benzene derivatives containing more than 2 isopropyl groups in their molecules, contacting said fraction with a silicate catalyst in admixture with at least an equimolar amount of either benzene or cumene or both benzene and cumene to effect transalkylation, and separating by distillation an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer from the resulting transalkylation product.

3. A process as claimed in Claim 1 or Claim 2, wherein para-di-isopropylbenzene is also removed from said alkylation product and subjected to isomerisation in the presence of a silicate catalyst to yield an isomerisation product from which an ortho- and meta-di-isopropylbenzenes fraction consisting substantially

entirely of the meta isomer is separated by distillation.

4. A modification of the process claimed in Claim 1 or Claim 2, which comprises contacting said fraction containing ortho- and meta-di-isopropyl benzenes and/or said fraction comprising benzene derivatives containing more than 2 isopropyl groups in their molecules with a silicate catalyst in admixture with at least an equimolar amount of either benzene or cumene or both benzene and cumene, to effect transalkylation and separating by distillation an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer from the resulting transalkylation product(s).

5. A process as claimed in Claim 4, wherein para-di-isopropylbenzene is also removed from said alkylation product and subjected to transalkylation in the presence of a silicate catalyst in admixture with at least an equimolar amount of benzene and/or cumene to yield a transalkylation product from which an ortho- and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer is separated by distillation.

6. A modification of the process claimed in Claim 1 or Claim 2, which comprises removing from said alkylation product: ortho- and meta-di-isopropylbenzenes, para-di-isopropylbenzene, and benzene derivatives containing more than 2 isopropyl groups in their molecules, either as 3 separate fractions or as one or more mixed fractions, contacting said separate or mixed fraction with a silicate catalyst to effect de-alkylation, and separating by distillation an ortho-and meta-di-isopropylbenzenes fraction consisting substantially entirely of the meta isomer from the resulting de-alkylation product(s)

7. A process for preparing meta-di-isopropylbenzene substantially as hereinbefore described with reference to the examples.

8. Meta-di-isopropylbenzene when prepared by the process or modification thereof as claimed in any one of the preceding claims.

H. I. DOWNES,
Agent for the Applicants,
St. Helen's Court, Great St. Helen's,
London, E.C.3.

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